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Chemistry and Physics of Glass

ARPA Order No. 418, Amendment No. 9

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Contractor: Naval Research Laboratory

Date of Contract: 19 January 1971

Amount of Contract: $215,000

Contract Expiration Date: 19 January 1972

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During the recent quarter, the glass program has been concentrated in three areas: (1) the investigation of ion implantation and valence variation as surface compression strengthening techniques, (2) the completion of structural studies on vitreous SiO_2 and a continuation of x-ray and neutron diffraction measurements on GeO_2 and As_2S_3 and (3) computer analysis of fracture in a two dimensional A_2B_3 disordered network. In addition Bausch and Lomb, currently operating under a no cost extension of their contract, has succeeded in preparing up to 400 gram melts on the NRL low platinum content laser glass and has provided samples suitable for damage threshold tests at NRL.

The tensile strength measurements on our glass samples have been made using the biaxial flexure method (3 ball and piston) described in our previous reports. The ion implantation experiments have been conducted on high purity SiO_2 (Suprasil 1) disks with dimensions 1.25" diameter by 1 mm thickness. We now have the capability to irradiate the samples over their entire face. The silica samples show little evidence of any radiation-induced optical and ESR absorption. Boron, nitrogen and neon have been the principal ions implanted in the past three months since these were readily available to us on the NRL Van de Graaff. The implant energies have ranged from 60 keV to

3 MeV. Surface concentrations of the implanted species have typically been 10^{15} to $10^{18}/cm^3$. Although the more heavily doped samples appear to show some increase in strength ($\approx 20\%$), we have yet to obtain the dramatic rise that had been hoped for. By going to longer irradiation times, concentrations as high as $10^{20}/cm^3$ can be achieved. This may produce the type of surface compression that we are seeking. Fused silica tends to contract and densify under irradiation and it is conceivable that this effect nullifies the compression expected by ion implantation, especially at low doses. Once this radiation compaction process has saturated, the ion stuffing should dominate with the result being a rapid increase in compression with further dose. Both borosilicate and aluminosilicate glasses will soon be available for ion implantation and these do not tend to show the strong radiation induced contraction observed in fused silica.

Experiments have been conducted on providing strengthened glasses by producing a surface layer of copper ions which penetrates below the depths of normal microcracks, reducing the copper ions to the ductile metal, and finally overcoating the surface with additional copper. Copper is introduced by heating the glass in cuprous chloride vapor and the reduction is obtained by heating in hydrogen. Overlaying has not yet been attempted. Some uniform appearing copper

mirrors were obtained in early experiments, but a reproducible procedure for the production has not yet been obtained.

A large sample of the soda lime glass containing vanadium has been prepared to test the procedure of glass strengthening by valence variation. Disks of a size to fit the strength test apparatus have been cut, polished and surface reduced and are available for testing. The development of a glass containing vanadium in a reduced valence state has been initiated. Strengthening experiments with this glass will involve surface oxidation.

A few glasses have been prepared to determine whether some newly acquired sources of the raw materials sodium carbonate, calcium carbonate, and aluminum oxide would produce purer glasses. Neither the sodium carbonate nor aluminum oxide produced improvements, but a purified batch of calcium carbonate yielded a glass with a lower copper impurity derived luminescence than has any earlier source.

The NRL work over the past several years on the structure of SiO_2 is being submitted for publication. An analysis of the X-ray and neutron diffractions patterns of silica glass has revealed that this glass has greater atomic ordering than has been previously recognized.

The analysis of the data was faciliated by the introduction of special physical criteria and mathematical operations to optimize the accuracy of the radial distribution function. This resulted in a radial distribution function which is free from cut-off ripple, appropriate in appearance in the inner region where distances do not occur and which possesses anticipated values for the coordination numbers as implied by the areas under the inner peaks. Preliminary results on the glasses of GeO_2 and As_2Se_3 indicate that these materials also contain considerable short-range order.

Work is well under way on the dynamics of the A_2B_3 glass-like disordered network in two dimensions. Computer programs have been written to generate the system (i.e., the Cartesian coordinates of every atom in the network), to set up the dynamical matrix for a particular choice of force constants and reduce it to tridiagonal form and to calculate the vibrational spectrum and eigenvectors for selected frequencies. Spectra computed for the layer-type chalcogenide glasses As_2S_3 and As_2Se_3 are in good agreement with the observed infrared and Raman spectra in both peak position and intensity, and the computation of eigenvectors for frequencies at absorption maxima will permit the assignment of the main characteristics of the spectra to specific vibrational modes. An effort is in progress to relate the

observed temperature dependence of the far-infrared absorption lineshapes of As_2Se_3 to changes in the width of the Gaussian distribution of As-Se-As bond angles.

Contract with Bausch and Lomb

The contract with Bausch and Lomb was extended until January 1, 1972 at no cost, and a further no cost extension of three months has been requested in order to provide an orderly completion of the work. Samples of the NRL developed laser glass as large as 400g have now been made. The elimination of bubbles remains a problem, but one batch melted at 1500°C was essentially bubble free. This melting temperature is 100° higher than the NRL recommendation. Since platinum contamination is a function of the melting temperature, the use of this temperature will be checked at NRL. Two glass samples were delivered from which small laser etalons can be fabricated, and on which passive tests of laser damage can be made. Future work is to continue the development of the glass melting procedure in order to eliminate bubbles and to provide samples one inch square by four inches long.

Publications

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Vacuum Ultraviolet Absorption in Alkali Doped Fused Silica and Silicate Glasses, G. H. Sigel, Jr. J. Phys. Chem. Solids <u>32</u>, 2373 (1971).

The Role of Alkali in the Formation of Radiation-Induced Defect Centers in Simple Silicate Glasses, G. H. Sigel, Jr. Proceedings of Ninth International Congress on Glass, Vol. 1, 801 (1971).

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<u>Bausch and Lomb</u>

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Optical Absorption of Lead in Glass, J. S. Stroud and E. Lell. J. Am. Ceramic Soc. <u>54</u>, (1971).